Novel Fission-Product Separation Based on Room Temperature Ionic Liquids

Huimin Luo,[1] Sheng Dai,[2] Peter V. Bonnesen,[2] and A. C. Buchanan, III[2]

[1]Nuclear Science & Technology Division and [2]Chemical Sciences Division, Oak Ridge National Laboratory

Robin D. Rogers,[3] John D. Holbrey[3] and Charles L. Hussey[4]

[3]University of Alabama and [4]University of Mississippi

Research Objectives

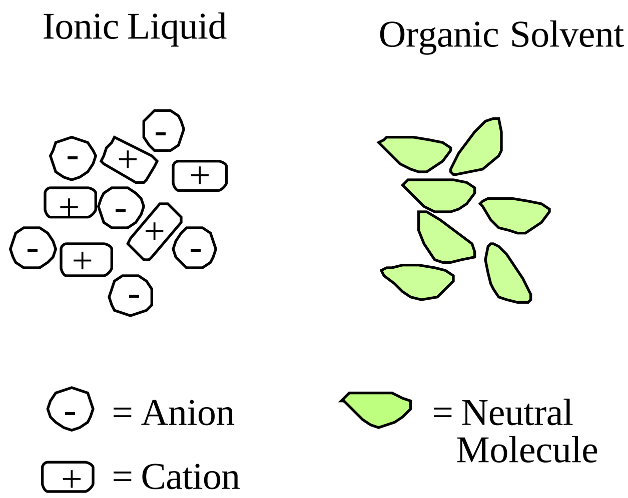
The overall goal of this project is to develop a new ionic liquid based solvent extraction process for separation of Cs-137 and Sr-90 from tank wastes.

- **To synthesize new ionic liquids tailored for the extractive separation of Cs^{+} and Sr^{2+}.**
- **To select optimum macrocyclic extractants through studies of complexation of fission products with macrocyclic extractants and transport in new extraction systems based on ionic liquids.**
- **To develop efficient processes to recycle ionic liquids and crown ethers via electrochemistry.**
- **To investigate chemical stabilities of ionic liquids under strong acid, strong base, and high level radiation conditions.**

Why Ionic Liquids?

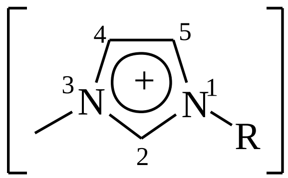
Ionic systems consisting of salts that are liquid at ambient temperatures can act as solvents for a broad spectrum of chemical species.

- ***Nonvolatility***
- ***Ionicity***
- ***Tunable Hydrophobicity***
- ***Tunable Lewis Acidity***
- ***Large Electrochemical windows***
- ***Thermal Stability***
- ***Nonflammability***
- ***Wide Liquid-Phase Temperature.*** (-100^{0}C to around 300^{0}C)

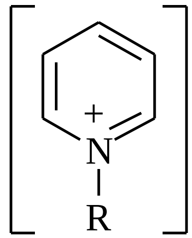


Range of Organic Cations and Anions Typically Used to Prepare Room-Temperature Ionic Liquids

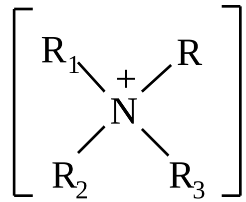
Most commonly used cations:



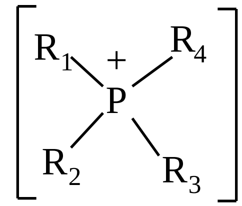
1-alkyl-3-methyl-imidazolium



N-alkyl-pyridinium



Tetraalkyl-ammonium



Tetraalkyl-phosphonium

($R_{1,2,3,4}$ = alkyl)

Some possible anions:

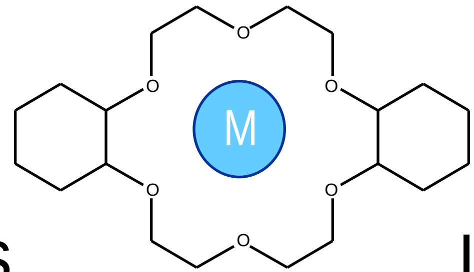
water-insoluble → water-soluble

water-insoluble		water-soluble
$[PF_6]^-$	$[BF_4]^-$	$[CH_3CO_2]^-$
$[(CF_3SO_2)_2N]^-$	$[CF_3SO_3]^-$	$[CF_3CO_2]^-$, $[NO_3]^-$
$[BR_1R_2R_3R_4]^-$		Br^-, Cl^-, I^-
		$[Al_2Cl_7]^-$, $[AlCl_4]^-$ (decomp.)

Most commonly used alkyl chains:

ethyl octyl
butyl decyl
hexyl

Comparison of Solvent Extractions Based on Molecular Solvents and Ionic Liquids



Molecular Solvents

M^{n+}(aq) D M^{n+}(org)   Unfavorable

n A^{-}(aq) D n A^{-}(org)   Unfavorable

crown(org) + M^{n+}(org) D {crown M^{n+}}(org)   Favorable

{crown M^{n+}}(org) + n A^{-}(org) D {crown M^{n+} nA^{-}}(org)
Formation of Ion Pair

Overall Process:
crown(org) + M^{n+}(aq) + n A^{-}(aq)
D {crown M^{n+} n A^{-}}(org)

Thermodynamically Unfavorable

Ionic Liquids (IL)

M^{n+}(aq) D M^{n+}(IL)   more favorable

n A^{-}(aq) D n A^{-}(IL)   more favorable

crown(org) + M^{n+}(IL) D {crown M^{n+}}(IL)   Favorable

M^{n+}(aq) + n Org^{+}(IL) D M^{n+}(IL) + n Org^{+}(aq)
Ion Exchange – Dietz & Rogers

Overall Process:
crown(IL) + M^{n+}(aq) + n A^{-}(aq) + n Org^{+}(IL)
D {crown M^{n+}}(IL) + n A^{-}(IL) + n Org^{+}(aq)

Thermodynamically favorable

Summary of Completed Research

- **Development of Highly Selective Extraction Process for Cs^+ Based on Calixarenes**
- **Demonstration of Facilitated Sacrificial Ion-Exchange Extraction Processes to Reduce the Loss of ILs and to Increase Extractive Strength of ILs**
- **Development of Recyclable IL-Based Extraction Systems**
- **Optimization of Selectivities of Extractants via Systematic Change of ILs**
- **Development of an Electrochemical Method for Recycling the Ionic Liquid-ionophore Extractant Phase Following the Extraction of Cs^+ and Sr^{2+}**
- **Synthesis of New Ethylene-Glycol Functionalized Bis-Imidazolium Ionic Liquids and Sr^{2+}/Cs^+ Partitioning Studies**

Anal. Chem. 2004, 76, 2773-2779.
Anal. Chem. 2004, 76, 3078-3083.

Comparison of Sr-Extraction Results Obtained Using Ionic Liquids and Conventional Solvents.

Extract Phase	K_d [a] *With 0. 15 M crown ether*[a]	K_d *Without crown ether*
$BuMe_2ImPF_6$	4.2	0.67
$BuMeImPF_6$	2.4×10	0.89
$EtMe_2ImTf_2N$	4.5×10^3	0.81
$EtMeImTf_2N$	1.1×10^4	0.64
$PrMe_2ImTf_2N$	1.8×10^3	0.47
$PrMeImTf_2N$	5.4×10^3	0.35
$C_6H_5CH_3$	7.6×10^{-1}	nm [a]
$CHCl_3$	7.7×10^{-1}	nm

14,000
Enhancement

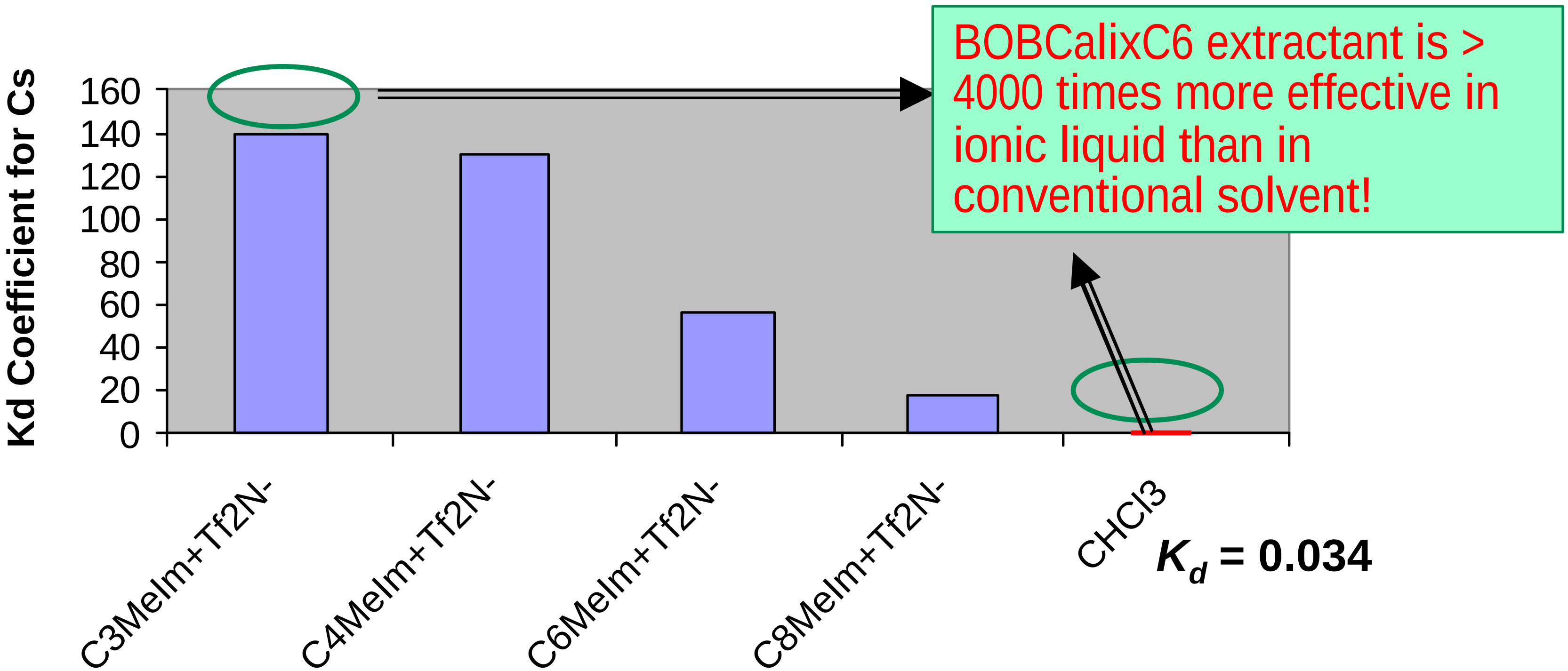
Messages:
- Key Role Played By Crown Ether
- Ion-Exchange Effect

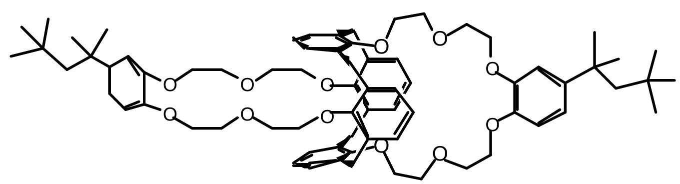
[a] The crown ether used in this experiment is dicyclohexane-18-crown-6.
[b] nm : not measurable.

S. Dai, Y. H. Ju, and C. E. Barnes "Solvent extraction of strontium nitrate by a crown ether using room-temperature ionic liquids" J. Chem. Soc. Dalton Trans. 1999, 1201-1202.

S. Dai, Y. H. Ju, and H. Luo, "Separation of Fission Products Based on Ionic Liquids" in International George Papatheodorou Symposium, Patras Science Park, 1999, p254-262

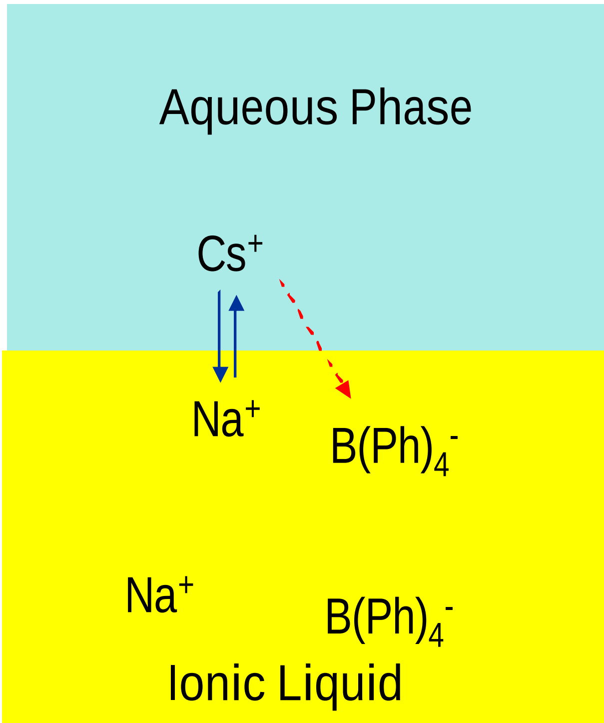
Very High Capture of Cesium Measured for Ionic Liquid-Based Solvents Containing BOBcalixC6





Calix[4]arene-bis(*tert*-octylbenzo-crown-6)
"BoBCalixC6"

Separation Systems Based on Facilitated Ion-Exchange Recognition



Facilitated Transport via Ion-Exchange Recognition

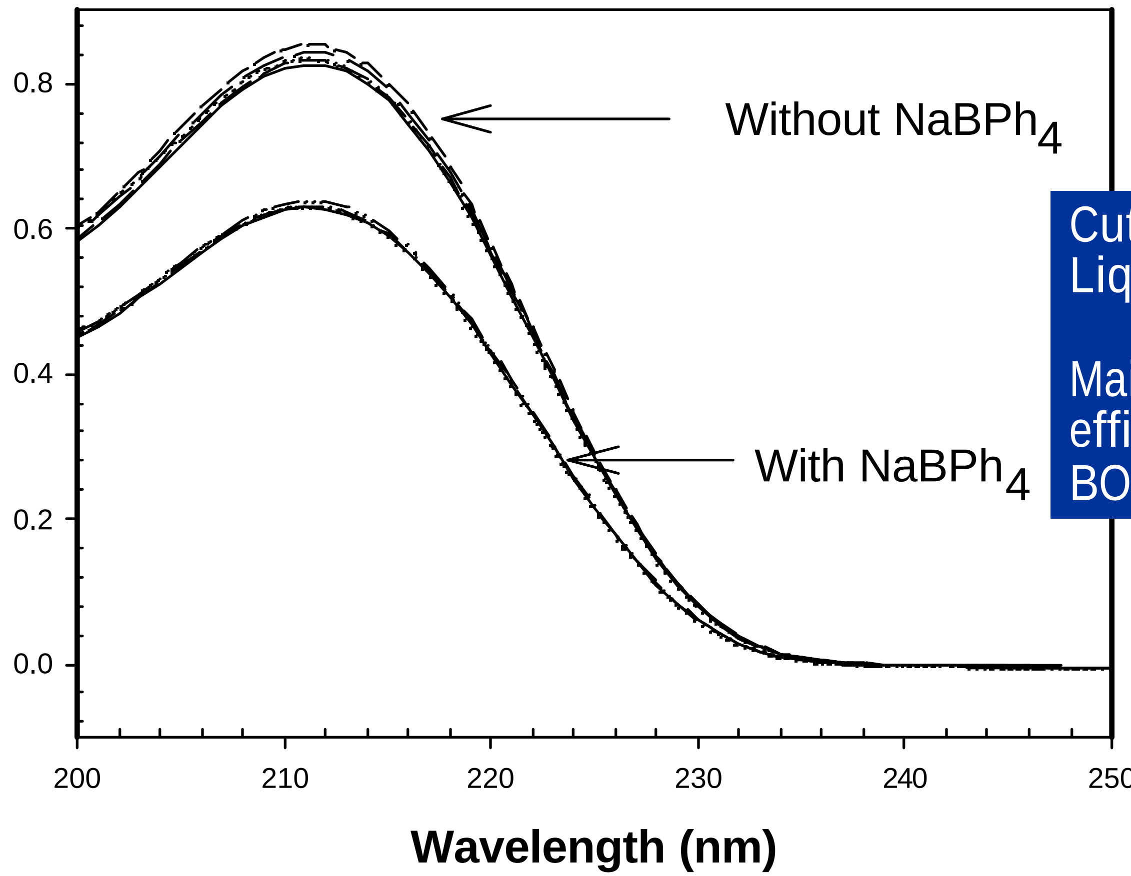
Liquid Membranes Containing $NaB(Ph)_4$ or $NaB(Ph\text{-}F_4)_4$ in Ionic Liquids

$NaB(ph)_4$	K_d (Cs)	Initial CsCl Concentration
7.69×10^{-3} M	0.21	88 ppm
2.34×10^{-3} M	0.32	320 ppm

$NaB(ph\text{-}F_4)_4$	K_d (Cs)	Initial CsCl Concentration
1.85×10^{-2} M	0.65	88 ppm
5.87×10^{-2} M	0.71	88 ppm

Na^+
Sacrificial Ion Exchanger

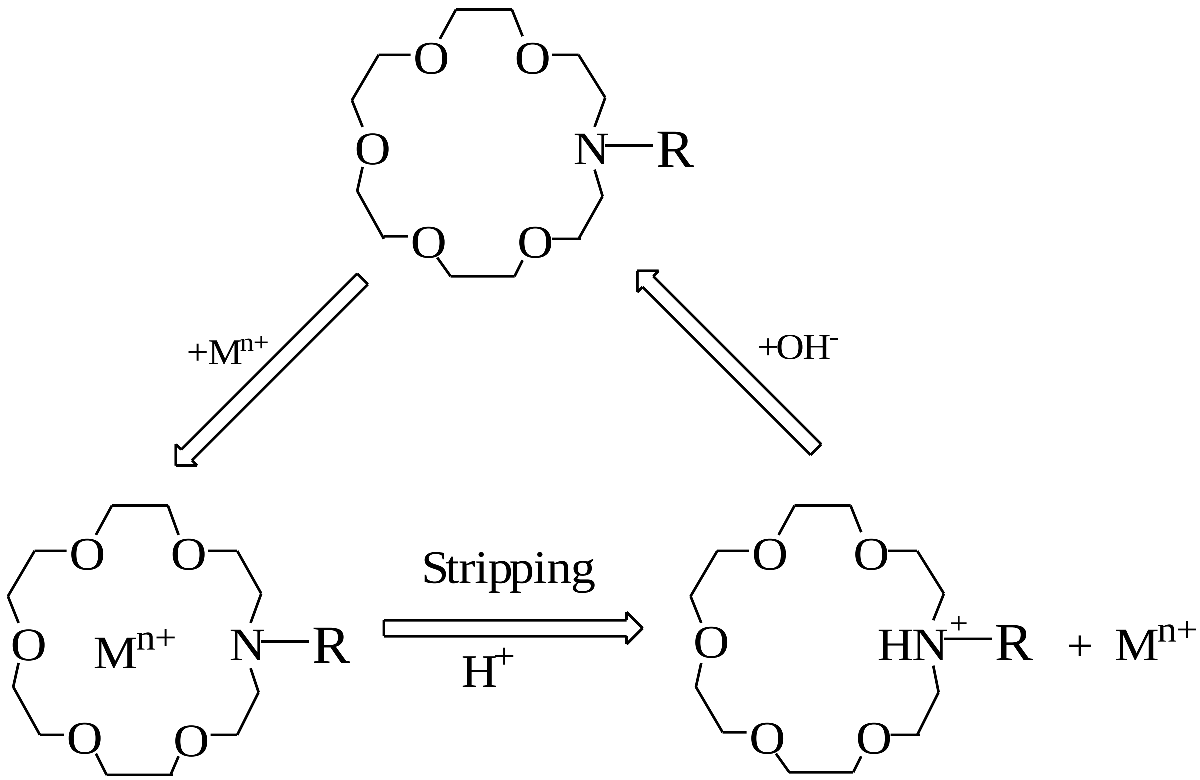
UV-Visible Spectra of Ionic Liquids Lost to Aqueous Solutions During Extraction with and Without $NaBPh_4$



Cut Loss of Ionic Liquid by 20%

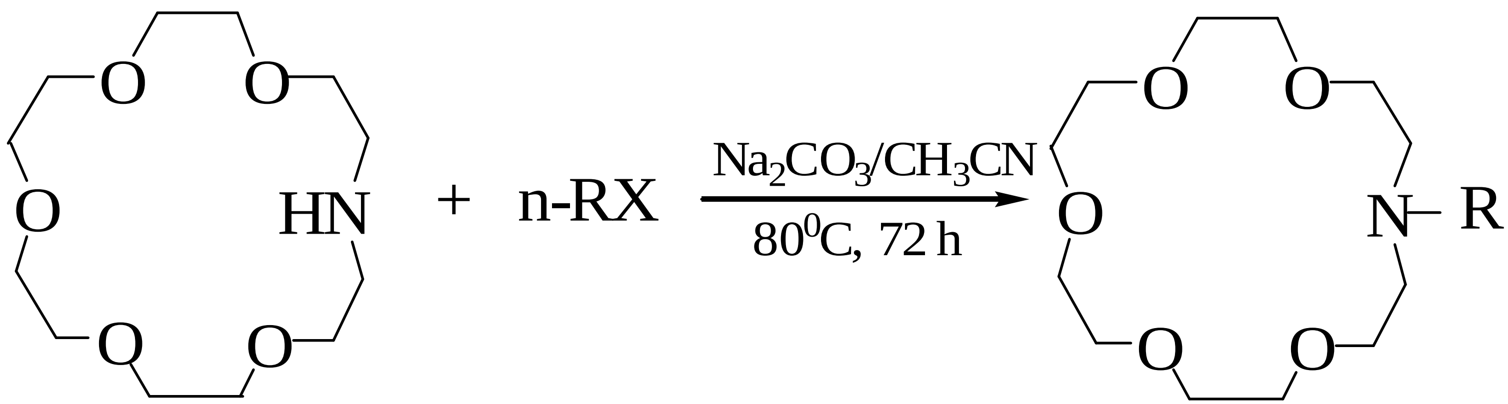
Maintain extraction efficiencies for BOBCalixC6

Development of Stripping Protocol to Recycle Macrocyclic Extractants



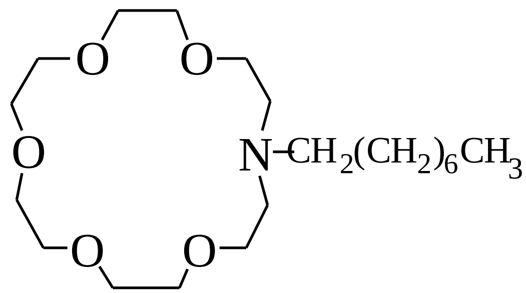
Luo, H.; Dai, S.; Bonnesen, P. V. *Anal. Chem.* 2004, in press

Synthesis of 1-Aza-18-crown-6 Derivatives



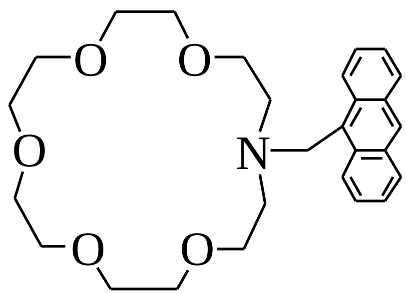
1. R = ethyl, X = Br
2. R = n-butyl, X = Br
3. R = n-hexyl, X = Br
4. R = n-octyl, X = Br
5. R = n-dodecyl, X = Br
6. R = n-hexadecyl, X = Br
7. R=$CF_3(CF_2)_5CH_2CH_2$-, X = I
8. R = 9-anthracenylmethyl, X = Cl

Recycling Experimental Results of Recyclable N-Alkylaza-18-crown-6 in $[C_4mim][NTf_2]$



$K_{dSr^{2+}}$=918.64, 1 drop 6N HNO_3 gave 100% Sr^{2+} recovery

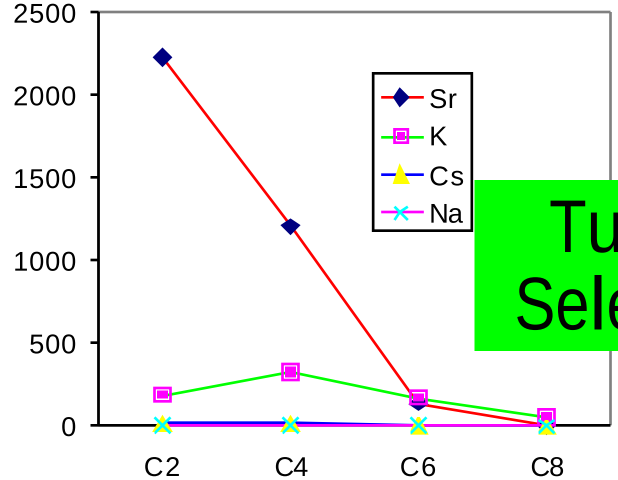
$K_{dCs^{+}}$=23.96, 1 drop 6N HNO_3 gave 100% Cs^{+} recovery

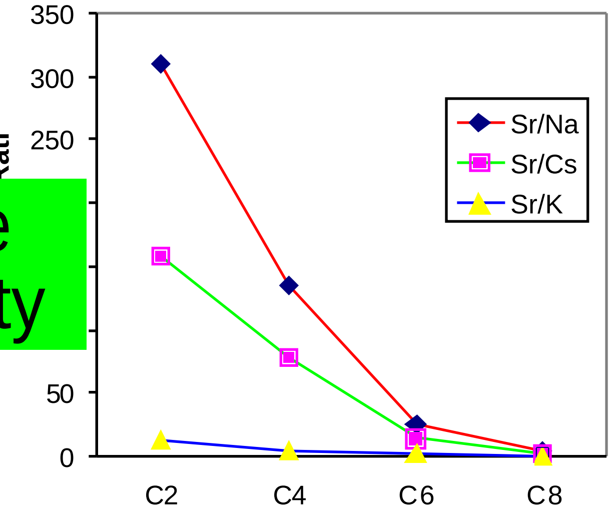


$K_{dSr^{2+}}$=3.77, 1 drop 6N HNO_3 gave 95% Sr^{2+} recovery

$K_{dCs^{+}}$=14.9, 1 drop 6N HNO_3 gave 100% Cs^{+} recovery

Effect of 1-Akyl Group of ILs on Efficiency and Selectivity of Competitive Sr, K, Na, Cs Cation Extraction from Aqueous Solutions into ILs Containing 1-Octyl-aza-18-crown-6



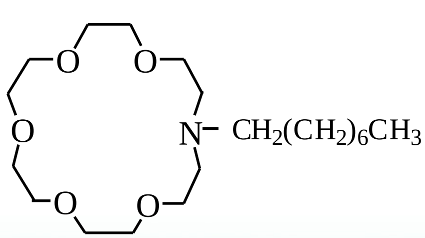


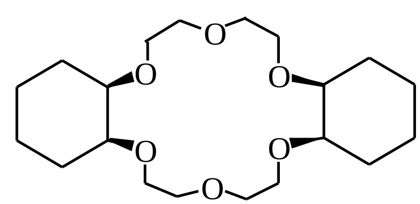
Tunable Selectivity

- **For C_2mim-Tf_2N & C_4mim-Tf_2N, the extraction efficiency is Sr^{2+}>>K^+> Cs^+>Na^+.**
- **In C_6mim-Tf_2N & C_8mim-Tf_2N, the order is K^+> Sr^{2+}> Cs^+>Na^+.**

Comparison of Extraction Results of 1-Octyl-aza-18-crown-6 with DCH18C6

OAZ18C6	DCH18C6
Recyclable	Non-recyclable
Non-commercial available	Commercial available
D_{Sr} : 8426 (in C_2) and 1072 (in C_4) D_{Cs} : 25.21 (in C_2) and 25.73 (in C_4)	D_{Sr} : 10734 (in C_2) and 935 (in C_4) D_{Cs} : 589 (in C_2) and 380 (in C_4)
Extraction Selectivity: $Sr^{2+} > K^{+} > Cs^{+} > Na^{+}$	Extraction Selectivity: $K^{+} > Sr^{2+} > Cs^{+} > Na^{+}$

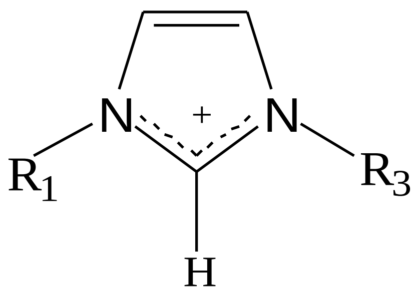




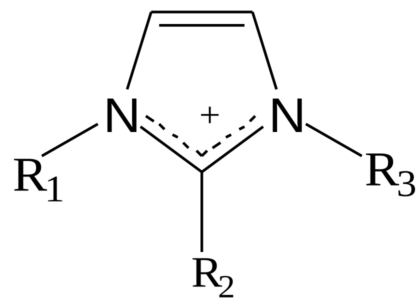
Future Research Plans

1. Synthesis and Optimization of ILs Tailored for Solvent Extraction of Fission Products
2. Synthesis and Study of Recyclable Crown Ethers
3. Optimization of Anions of ILs for Extraction of Fission Products
4. Sacrificial Ion-Exchange Method for Synergistic Extraction of Metal Ions and Reduction of ILs Loss
5. Development of an Electrochemical Method for the Non-Destructive Removal of Extracted Cs^{+} and Sr^{2+}
6. Study of Stabilities of ILs in Harsh Chemical and Radiation Environments

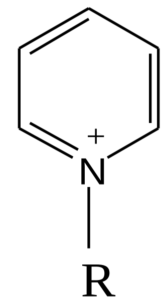
Synthesis and Optimization of Ionic Liquids Tailored for Solvent Extraction of Fission Products



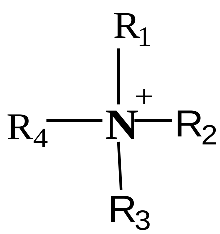
1,3-Dialkylimidazolium-Based



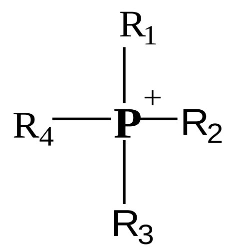
C(2)-Position Substituted Imidazolium-Based



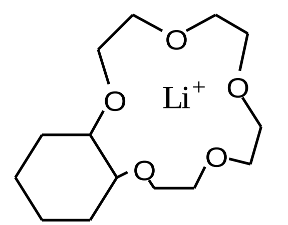
Pyridinium-Based



Quaternary Ammonium-Based

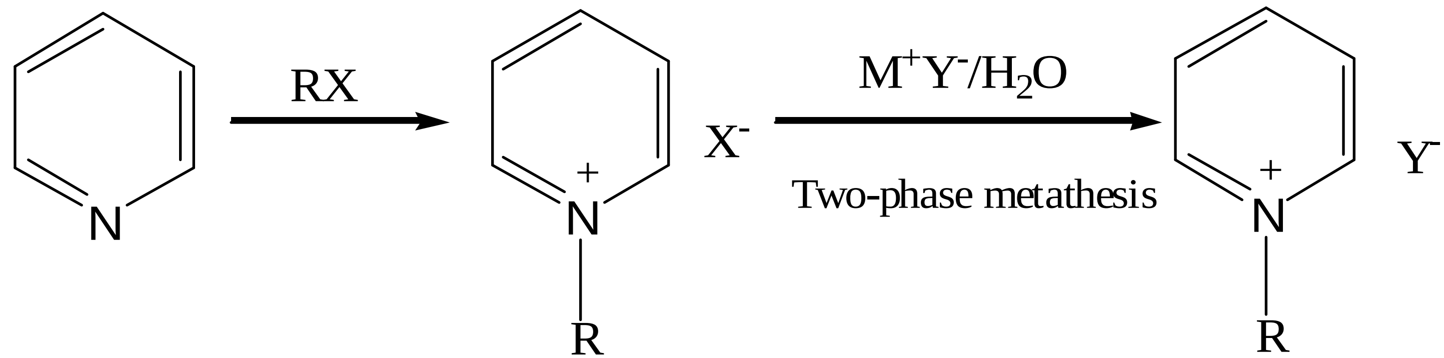


Tetraalkyphosphonium-Based



Metal Complexes-Based

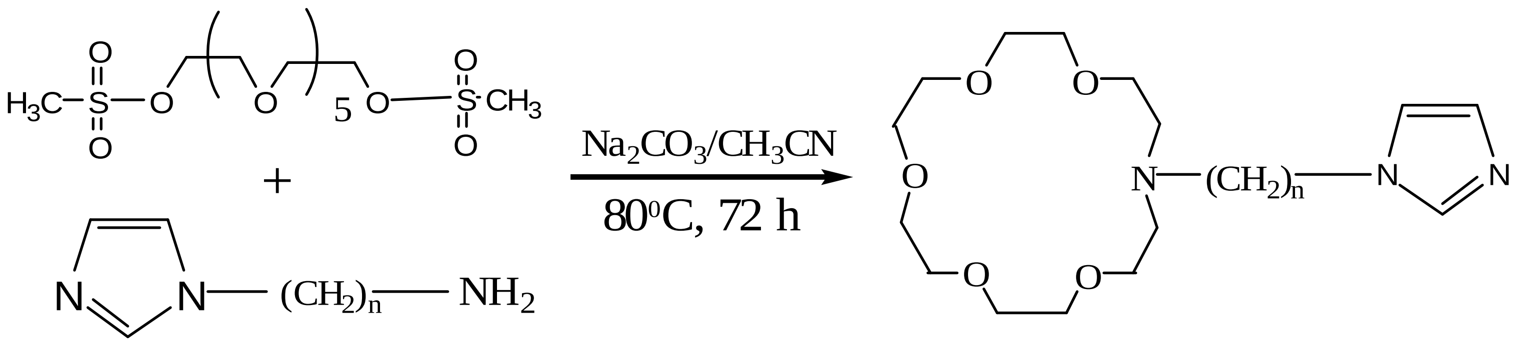
Typical Synthesis of Ionic Liquids Based on Alkylpyridium and Quaternary Ammonium

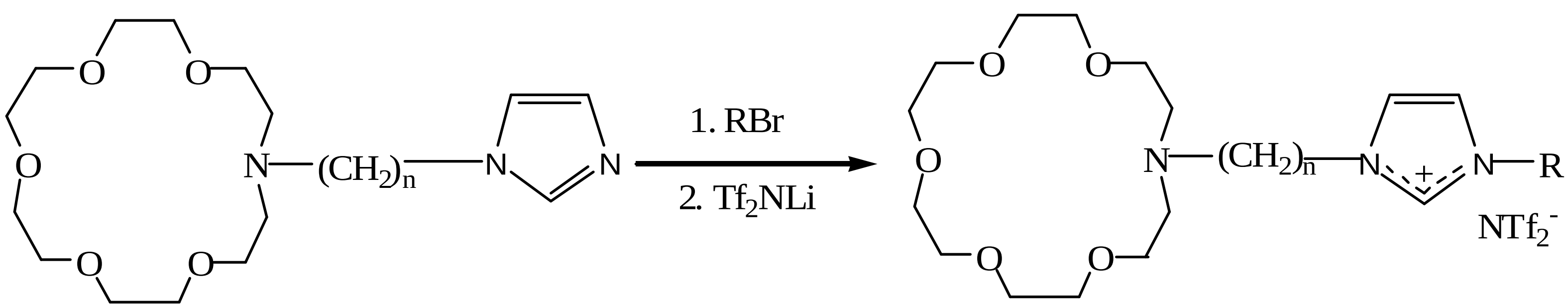


$$\mathrm{R'R_2N} \xrightarrow[\mathrm{CH_3CN}]{\mathrm{R''I}} \mathrm{R'R_2R''NI} \xrightarrow[\mathrm{H_2O}]{\mathrm{LiNTf_2\ or\ LiBETI}} \mathrm{R'R_2R''N^+NTf_2^-}\ \text{or}\ \mathrm{R'R_2R''N^+BETI^-}$$

$$\mathrm{RNH2} \xrightarrow[\mathrm{KOH}]{\mathrm{CH_3I}} \mathrm{(CH_3)_3RNI} \xrightarrow[\mathrm{H_2O}]{\mathrm{LiNTf_2\ or\ LiBETI}} \mathrm{(CH_3)_3RN^+NTf_2^-}\ \text{or}\ \mathrm{(CH_3)_3RN^+BETI^-}$$

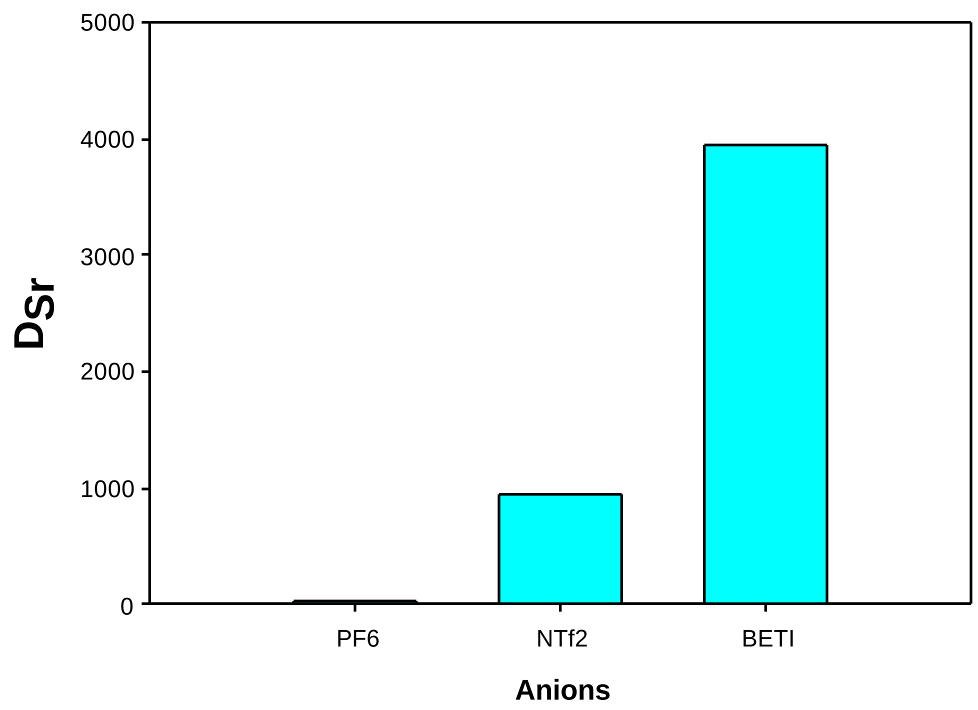
Synthesis of Task-Specific Ionic Liquids Containing an Aza crown Ether Fragment





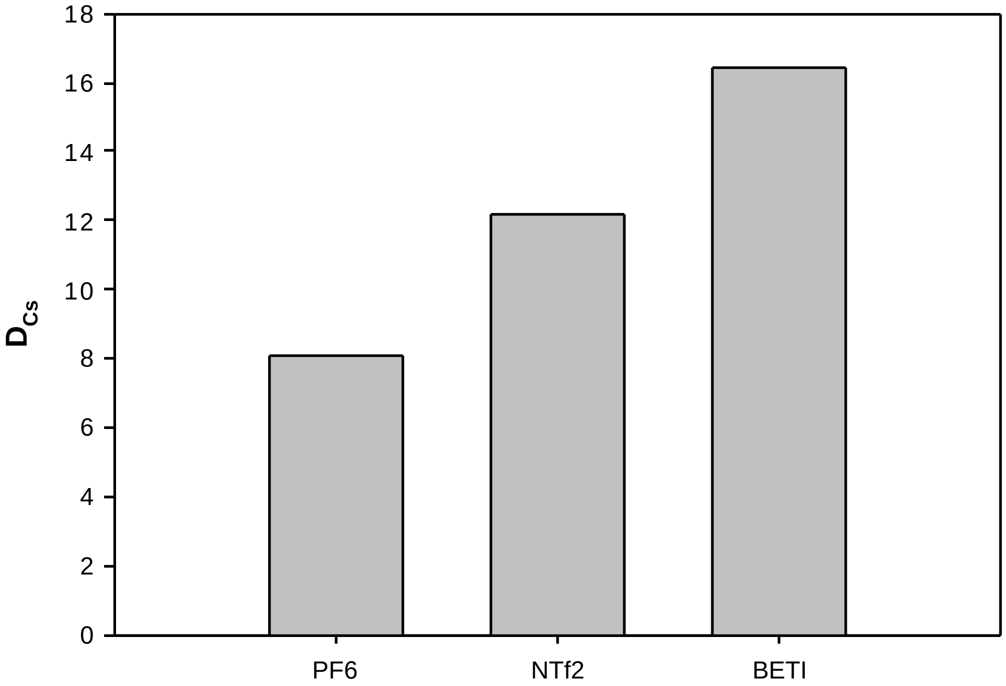
Dependence of D_{Sr} on IL Anions of [C_4mim]-based ILs Containing DCH18C6.

- **D_{Sr} value increases dramatically as the anion changed from PF_6 to NTf_2 to BETI. D_{Sr} for BETI is more 200 times larger than that for PF_6.**
- **The increase of D_{Sr} with the hydrophobicity of the counter anions is in sharp contrast to the observation with the cation effect of ILs. In the latter case, D_{Sr} decreases with the hydrophocity of the IL cations.**



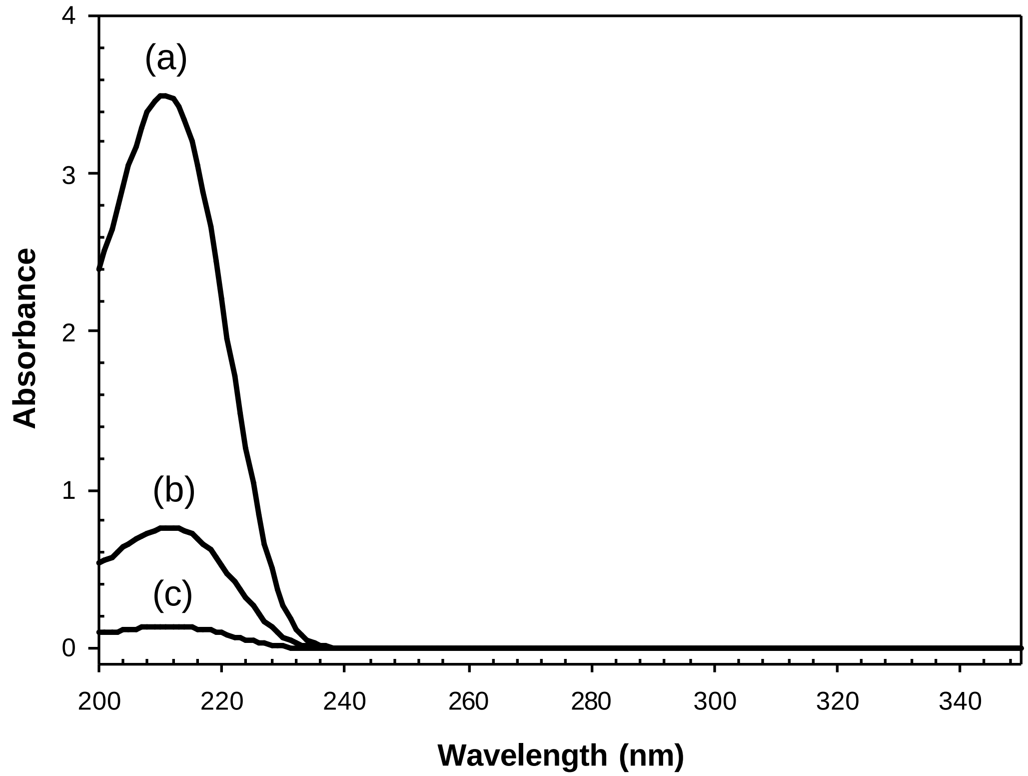
Anion Effect on D_{Cs} of $[C_4mim][X]$ Containing BOBCalixC6

- D_{Cs} values increase slightly as the anion changed from PF_6 to NTf_2 to BETI.

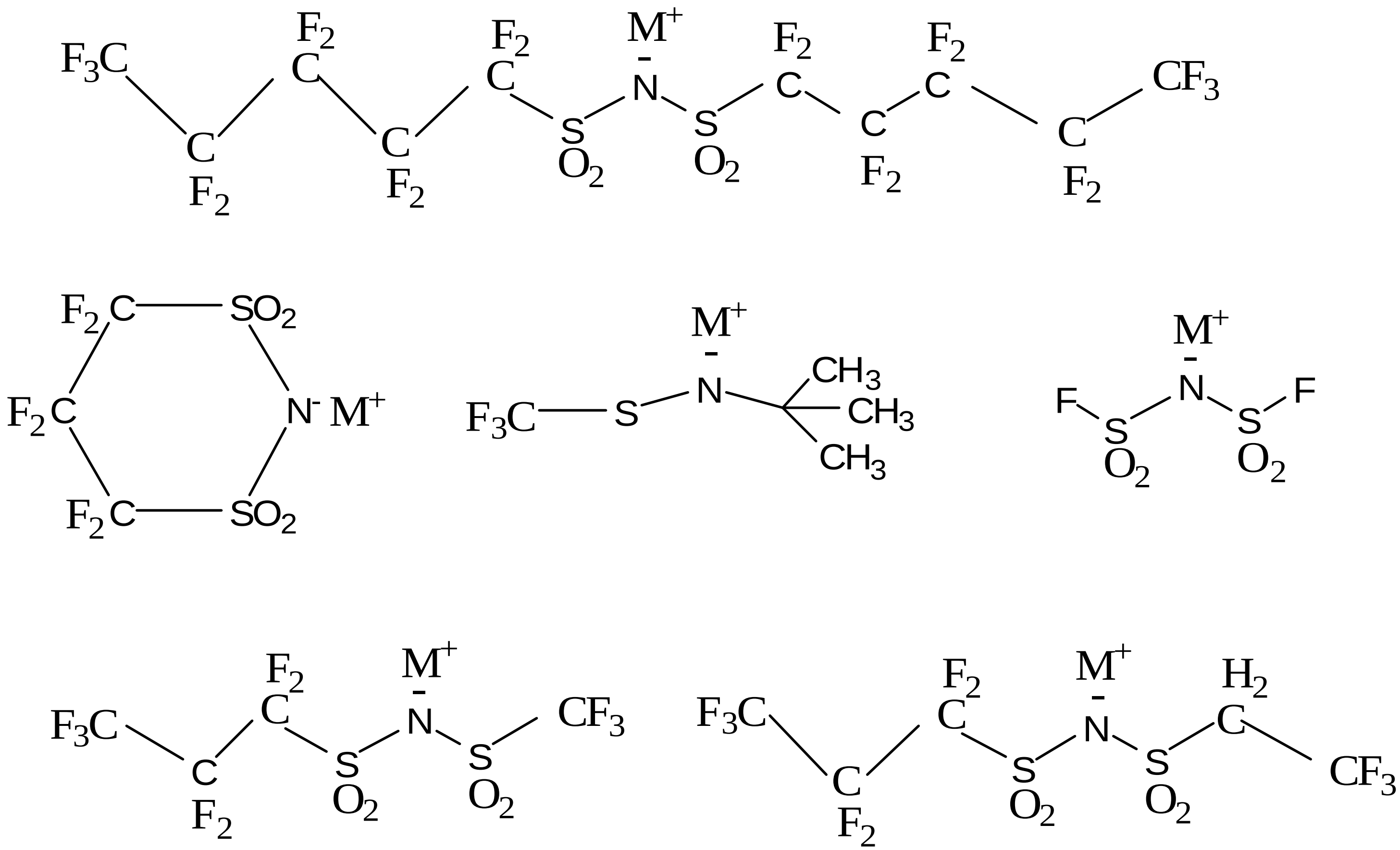


Detection of Cation Leaching of (a) [C4mim][PF6], (b) [C4mim][NTf2], and (c) [C4mim][BETI] via UV-Vis Spectra of Equilibrium Aqueous Phases

- **The loss of the ILs was found to be strongly correlated to the conjugate anions. The more hydrophobic the anions are, the less are the losses of the ILs. The loss of C_4min-BETI is about 25 fold less than that of C_4min-PF_6.**



Examples of Alkaline Metal Salts Can be Used to Produce a Variety of Ionic Liquids



Proton-Based Sacrificial Ion Exchangers

$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$

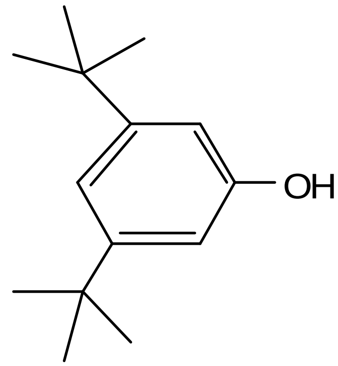
oleic acid

pKa: 4.8

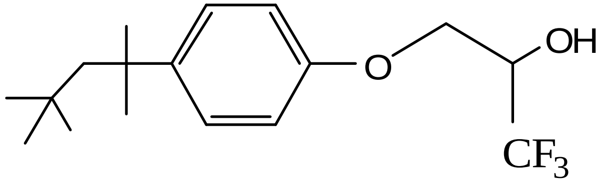
$HF2C(CF2)_7CH_2OH$

$CH_3(CH_2)_7OH$

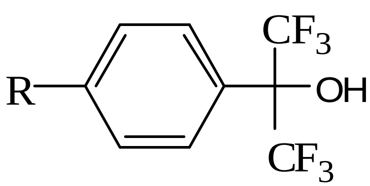
pKa: 20



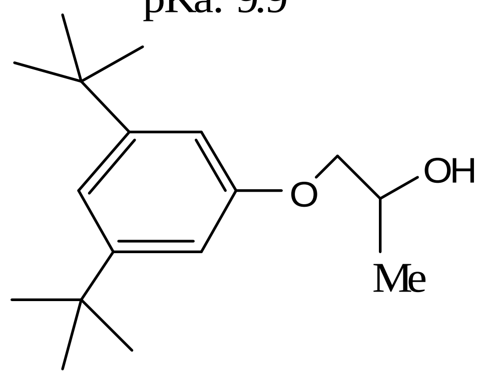
pKa: 9.9



pKa: 12.5



pKa: 8.8



pKa: 12.5

Moyer, B. A., etc. *Anal. Chem.* **2003,** 405

Effect of Carbon Chain Length of ILs and Synergistic Effect of Oleic Acid and Two Different Hydroxy Acids on Extraction Results of Rmim-Tf_2N Containing DCH18C6

Aq. Phase	Crown Ether	ILs containing Proton Exchanger	R in Rmim-Tf_2N			
			Ethyl, C2	Butyl, C4	Hexyl, C6	Octyl, C8
$SrCl_2$	DCH18C6 0.02 M	NO	465.4	74.08	15.14	2.06
		Oleic acid(1)	466.3	136.7	16.64	2.22
		Fluoro-(2)	465.9	64.3	15.85	1.82
		Di-tertbutylphenol (3)	419.0	58.7	12.48	1.71

ACKNOWLEDGEMENT

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